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Chemical characterization of stratus cloudwater and its role as a vector for pollutant deposition in a Los Angeles pine forest

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ABSTRACT

Highly concentrated, acidic stratus cloudwater was monitored as it intercepted a pine forest (Henninger Flats) 25 km northeast of Los Angeles. Observed pH values ranged from 2.06 to 3.87 for over 100 samples collected in 1982 and 1983 with a median value below pH 3. The ratio of nitrate/sulfate in cloudwater samples was between 1.5 and 2; rainwater at the same site had a ratio of approximately 1. The solute deposition accompanying several light, spring rains (summing to ~1% of annual rainfall) was a disproportionate fraction of the annual total: H^+, NO_3^- and SO_4^{2-} were ~20% or more. Based on a reasonable estimate of fog precipitation, deposition of sulfate, nitrate and free acidity due to intercepting stratus clouds may be of comparable magnitude as that due to the incident rainfall at Henninger Flats.

Cloudwater that had deposited on local pine needles was collected. It was in general more concentrated than ambient cloudwater but with comparable acidity. Enrichment of K^+ and Ca^{2+} in those samples and in throughfall is believed to be due to leaching from foliar surfaces. Injury to sensitive plant tissue has been noted in the literature when prolonged exposure to this severe kind of micro-environment has been imposed.

1. Introduction

In addition to the orographic enhancement of precipitation at mountain sites, cloud droplet capture can lead to greater pollutant deposition relative to the surrounding lowlands. Fog-derived (sometimes called mist or "occult") precipitation has been determined to be an important hydrological input to some ecosystems (Kerfoot, 1968). Also, measurements of cloudwater composition have shown it to have higher aqueous-phase concentrations compared to precipitation at the same locale (Mrose, 1966; Okita, 1968; Munger et al., 1983b). These two factors combine to suggest the potential for significant pollutant deposition in mountain forests impacted by frequent cloud interception. Often omitted from mass-balance calculations or regional monitoring, this pathway may represent an important component of the total deposition. By accelerating removal of local emissions, this may be especially significant in urban-impacted environments.

Enhanced precipitation in coastal and mountain forests has been reported for collectors located beneath trees exposed to fog-laden wind. Topography, leaf shape and total area, and canopy structure are important parameters (Kerfoot, 1968). In an early study of fog interception in Japan (Yosida, 1953), an average fogwater deposition rate of 0.5 mm h^{-1} was reported for a coastal forest. Oberlander (1956) measured between 45 and 1500 mm of fog-derived precipitation in less than 6 weeks on the San Francisco peninsula with collectors beneath 5 trees. Although it did not include the frequency or duration of fog,

that study underscored the magnitude of water flux and emphasized the importance of location in addition to the height of the trees in affecting fog-derived precipitation. A number of investigators have employed artificial foliar collectors (Schlesinger and Reiners, 1974) or screen "fog-catchers" (Nagel, 1956; Ekern, 1964; Vogelmann et al., 1968; Vogelmann, 1973; Azevedo and Morgan, 1974) to measure the enhancement of water catchment by horizontal interception. Because of their relatively small interception cross-sections, these collectors may underestimate the flux of fog precipitation induced by the actual forest canopy. The fog-derived precipitation in these studies represented a significant fraction of the total water flux—up to several times the measured incident rainfall.

Following the incorporation of aerosol and gaseous species into cloud and fog droplets, dissolved pollutant species may be brought into contact with vegetative surfaces. The chief mechanisms for deposition are impaction, sedimentation—both strongly enhanced by increased particle inertia—and turbulent transport. Damage to sensitive plant tissue and other elements of the biota caused by direct exposure to aqueous acids has been the subject of field and laboratory research (e.g. Tukey, 1970; Evans, 1982). Cases of specific injury and growth retardation have been reported for several plant and tree species in exposure studies (Wood and Bormann, 1974; Haines et al., 1980; Scherbatskoy and Klein, 1983) with threshold for effects generally noted in the range of pH = 2 to 3.

Our objectives were to characterize the chemical composition of stratus cloudwater and to address the potential that droplet capture may play as a vector for pollutant deposition. In this paper, we report the composition of rainwater, cloudwater, aerosol, bulk deposition, and throughfall samples collected in a Los Angeles pine forest. These are used to compare the relative contributions by these various deposition pathways. Interception of stratus clouds on the mountain slope is evaluated for its role in enhancing pollutant deposition. Our findings are presented as a measure of regional pollution not generally monitored. We also report the composition of deposited cloudwater collected from pine needles. These data are discussed in terms of chemical interactions occurring at the vegetative surfaces.

2. Experimental

Our monitoring site was located at Henninger Flats, a campground and tree nursery located at approximately 780 m MSL on the southern slope of Mount Wilson, 25 km northeast of Los Angeles Civic Center. The site is shown in elevation and plan views in Fig. 1. During the spring and early summer, stratus clouds are common along coastal California, associated with the persistent marine layer (Keith, 1980). An inversion base forms the top of the stratus deck. When drawn inland by an onshore pressure gradient, these low-lying clouds can intercept coastal mountain slopes, leading to frequent, dense fog at elevated sites from late evening through morning hours.

Cloudwater was collected on 8 days in June 1982 and 15 days in May and June 1983. On two of the sampling dates in May 1983, the cloud top was below Henninger Flats, and cloudwater was collected 100–200 m downslope. On most dates sampling proceeded from the time cloud had intercepted the site to the time the fog had dissipated. When fog occurred at the site, it was usually preceded by a relatively strong onshore breeze. The local, nighttime drainage flows inherent to the topography also affected the fog characteristics. Note: we refer to the phenomenon as fog at the site; however on the regional scale, the mountain slope was intercepted by stratus clouds. Hence, we refer to our samples as cloud-, rather than fogwater.

A Caltech rotating arm collector (RAC) was used to collect cloudwater (Jacob et al., 1984b). In essence, the RAC is a rapidly rotating (1700 rpm) propeller with slots and collection bottles located on both ends. The axis of the rotating arm was 1.4 m above ground level. The collector was situated approximately 200 m back from the ridge in a gently sloped, open area, surrounded by dense and tall (30 m) vegetation (Fig. 1). The external collection surfaces of the RAC minimize collection losses for large droplet sizes. Because of the collector design and the rapidity in which impacted droplets are removed from the slots to the bottles, evaporation of collected cloudwater is not a problem. Model-scale calibration of the collector design using solid particles has indicated the lower size-cut (50% collection efficiency) to be approximately 20 μm diameter (Jacob et al., 1984b). Little research has been conducted to determine size-

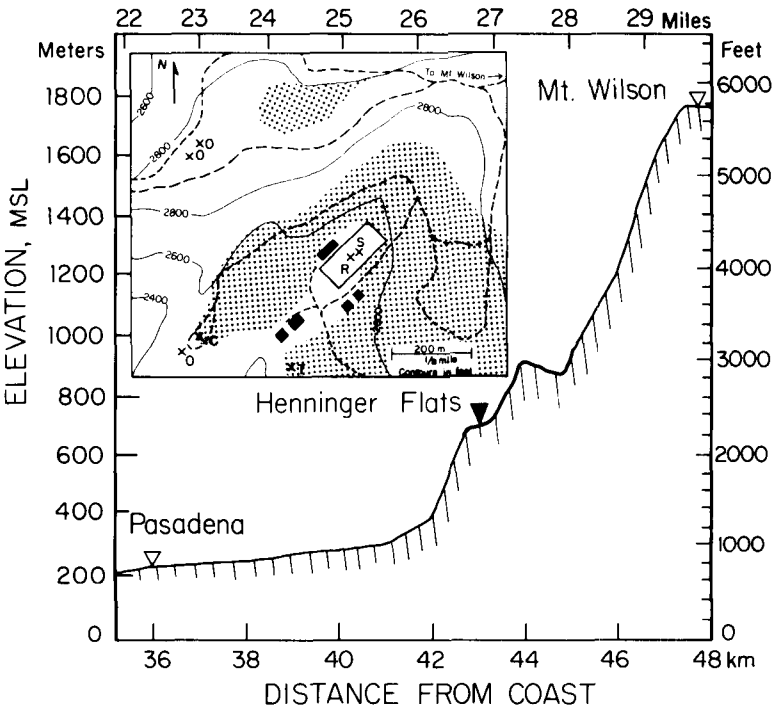

Fig. 1. Profile of southwestern Mount Wilson slope showing location of sampling site. Los Angeles Civic Center is located at 24 km from Pacific Ocean along same profile. On site plan (insert), S is cloudwater sampling site in nursery; R is rainwater collector location; O and C are open (bulk) and canopy (throughfall) bucket collectors; and T is location of tree drop samples. Shading indicates dense pine forest vegetation; dashed lines are dirt roads.

composition relationships of the cloud droplet spectrum experimentally. However, during an intercomparison of fogwater collectors at Henninger Flats (Hering and Blumenthal, 1984), the RAC samples gave consistently very good agreement with those of a jet-impactor having a lower size-cut measured between 2 and 5 μm diameter (Katz, 1980). Hence, the concentrations of the smaller droplets was not sufficiently different to alter the overall composition of simultaneously collected samples.

Sampling intervals generally ranged from 30 to 60 minutes; sample volumes were usually 10–30 ml, although some as small as 1 ml were analyzed. The RAC water collection rate has been found to correlate well with several independent methods (Hering and Blumenthal, 1984). Jacob et al. (1984b) reported that the theoretical RAC collection rate (5 m^3 min^{-1}) gave liquid water content (LWC) which was approximately 60% the value determined by total filter measurements made in radiation fog. For this study, RAC-derived LWC values were calculated with this empirical correction factor:

$$\text{LWC} = \frac{\text{Sample volume}}{\text{Sample interval} \times \text{theoretical air volume sampling rate} \times 0.6}$$

In an environment where LWC greatly varies, temporally and spatially, the RAC-derived measurements have the advantage that they are collocated with each of the chemical samples and similarly time-averaged. This relationship gave good agreement with the other methods, except for patchy and dissipating fogs (Waldman, 1985).

Immediately after each sample was collected, pH was measured using a Radiometer PHM 82 meter and combination electrode; standard calibration of the electrode was performed at pH 7, 4 and 1.68. Within 30 minutes, aliquots were preserved from each sample for analysis of formaldehyde, S(IV)

and trace metals. For major ion determinations, aliquots were necessarily diluted from 5 to 50:1. Further details of fogwater sample handling and analytical protocols are presented elsewhere (Munger et al., 1983a).

In addition to cloudwater collection as in 1982, ambient aerosol measurents were made during the spring of 1983. Total and fine-fraction aerosol loadings were determined using 47 mm Teflon (Zefluor—1 μm pore size) filters sampling at 10 lpm. Samples—in dry and fog-laden air—were collected simultaneously on an open-faced filter (total) and behind a cyclone separator (fine <3 μm). The concentrations of water soluble ions were determined following aqueous extraction with a reciprocating shaker for 1 hour. Subsequent extractions of the filters produced satisfactory blanks.

Rainwater was monitored at the nursery from November 1982 to June 1983 using a wet-only collector (Liljestrand, 1980). Bulk deposition samples were collected between May and July 1983 in open, plastic buckets. On several occasions droplets that had accumulated on pine needles by cloud droplet capture were collected. This was done by manual, drop-by-drop removal. Selected trees were repeatedly sampled. Further details of these deposition measurements are given in separate sections.

3. Results and discussion

The objective of this field study was to determine the relative contributions of various pathways to the overall pollutant deposition. For clarity, a summary of cloudwater data is first presented and discussed. Several specific fog episodes are described. Wet and bulk deposition data sets are then presented. This is followed by calculations of the magnitude of fog-derived precipitation and the associated pollutant deposition based on the cloudwater composition reported. With these, a comparison of the pollutant fluxes associated with precipitation (incident and occult) and dry deposition pathways is given. Finally, the composition of intercepted cloudwater is presented with a discussion of its potential interactions with foliar surfaces.

3.1 *Cloudwater composition*

Summaries of 1982 and 1983 results for cloudwater and rainwater chemical analyses are presented in Table 1. For comparison, values are also given for the 1978–79 volume-weighted mean rainwater concentrations at Pasadena and Mount Wilson (225 and 1800 m MSL, respectively). For most species, the median values for Henninger Flats cloudwater concentrations are 20 or more times those for local rainwater. The ionic balances for cloudwater data are presented in Fig. 2. In general, the results for both years are satisfactory with 1983 data giving very consistent balance. Ionic balance was calculated as a check on both the analytical precision and the completeness of the ion determinations. We are confident that all the major ionic species have been measured. There were a few cases in the 1982 data set which gave poor ionic balance, these for samples with the highest acidities and concentrations (and the smallest sample volumes). For those samples, much of the worse imbalances could be explained by a small analytical error at low pH: e.g. at pH $\sim$ 2, d(pH) = $\pm$0·1 gives d[H$^+$] of $\pm$2500 μeq^{-1}. The better agreement for 1983 data was also due to our experience working with samples of such high concentrations. The protocol for the latter year included a single, quantitative dilution of each sample (5 to 50:1) rather than separate ones for the individual ion determinations, as for the 1982 samples.

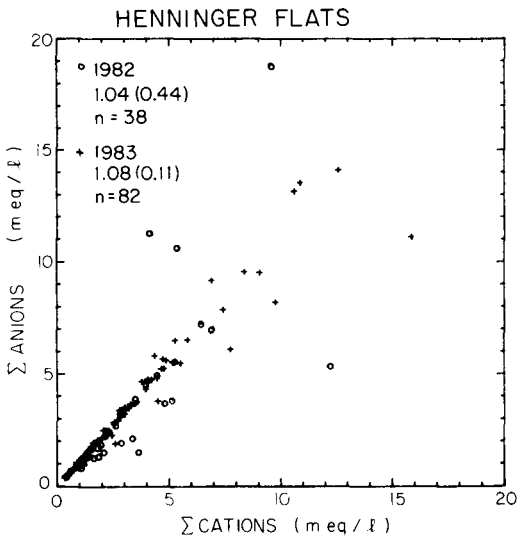

Fig. 2. Total anion versus cation concentrations for cloudwater samples of 1982 and 1983 with mean (std. dev.) of ion balances for n samples.

Table 1. *Median and range of concentrations for cloudwater samples-Henninger Flats: 1982 and 1983*

		Cloudwater		Rainwater		
		1982[a]	1983[b]	Site[c]	Pasadena[d]	Mt. Wilson[d]
pH		2.86	2.96	4.6	4.4	5.0
		2.06–3.65	2.07–3.87			
H^+	μeq l^{-1}	1365	1100	24	39	10
		224–8710	135–8510			
Na^+		146	285	14	24	26
		5–2465	3–6320			
K^+		18	22	0.9	1.7	1.7
		1–161	3–197			
NH_4^+		576	582	9.2	21	36
		128–3130	62–7420			
Ca^{2+}		132	142	4.1	6.7	9.3
		5–975	3–3020			
Mg^{2+}		54	106	5.2	7.2	6.6
		2–762	1–1735			
Cl^-		125	220	18	28	28
		21–1965	15–9650			
NO_3^-		1435	1510	17	31	23
		191–9500	161–16,300			
SO_4^{2-}		617	971	19	39	40
		128–7310	133–9300			
S(IV)	μmol/l^{-1}	15	7	na	na	na
		7–85	0.4–94			
CH_2O		66	50	na	na	na
		34–920	12–173			
Fe	μg l^{-1}	1055	455	na	223	28
		200–6880	20–4800			
Pb		346	212	na	na	na
		80–2780	38–2500			

[a] Median and range for 38 samples (42 for pH) on 8 days.
[b] Median and range for 82 samples (86 for pH) on 15 days.
[c] Volume-weighted mean values for October 1982 to July 1983 (see Table 3).
[d] Volume-weighted mean values for 1978–79 (Liljestrand and Morgan, 1981).
na = not analyzed.

Hydrogen, ammonium, nitrate, and sulfate dominated the ionic composition in most samples; this is consistent with previous observations for Los Angeles aerosol (Appel et al., 1978). For most samples, non-sea salt sulfate was greater than 90% of measured sulfate, assuming as an upper limit that sodium was solely of marine origin. The nitrate-to-sulfate equivalent ratio for these samples was between 1.5 and 2 (Fig. 3). This ratio is similar to fogwater samples collected in the Los Angeles basin (cf. Munger et al., 1983a) but markedly different from local rainwater with ratios less than 1 (Table 1). The basinwide nitrate-to-sulfate equivalent ratio for precursor emissions has been reported between 2 and 3 (California Air Resources Board, 1979; 1982).

The low pH values in the cloudwater occurred in a rather narrow range: pH = 2 to 4 (Fig. 4). The degree to which ambient acids have been neutralized in the atmosphere following their formation is indicated by the equivalent ratio of $[H^+]$ versus $[NO_3^-]$ plus $[SO_4^{2-}]$. The ratio for Los Angeles stratus cloudwater was generally ~0.5 (Fig. 5). That is, in the cloudwater about half of the acidic anions were not neutralized.

Even for the cases with low aqueous concentrations, sufficient ambient bases were either not available or scavenged to fully neutralize the acid.

Gaseous ammonia should be completely scavenged by acidic cloud droplets (Jacob and Hoffmann, 1983). Basinwide, ammonia emissions are one-third of the SO_2 and NO_x sum on an equivalent basis; however, major source areas are located in San Bernadino and eastern Los Angeles counties (Russell et al., 1983). The degree of fractional acidity reported herein is similar to coastal fogs collected in southern California (Munger et al., 1983a). However, for sites with very high ammonia emissions (cf. Jacob et al., 1984a), fogwater with similarly high ionic concentrations of acidic anions were largely neutralized. For some of the highly concentrated cloudwater samples, $|Ca^{2+}|$ and $|Mg^{2+}|$ were 10–50% lower for filtered (0.2 μm pore size) compared to non-filtered aliquots. Na^+, K^+ and NH_4^+ showed little difference between aliquots. This suggests that some of these ions in the condensation nuclei do not rapidly or completely dissolve. That is, there may be a kinetic limitation to the neutralization of cloudwater by the dissolution of an alkaline fraction.

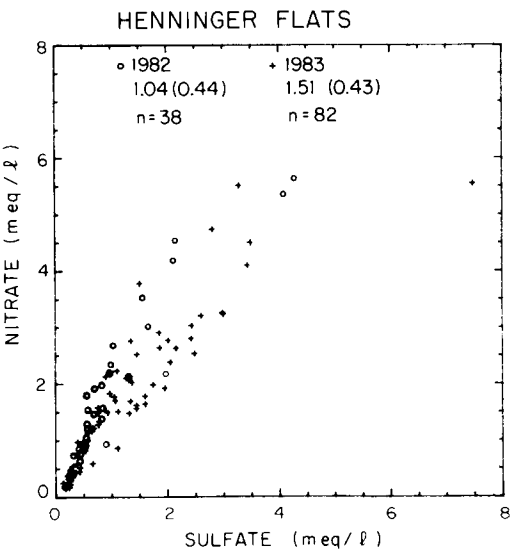

Fig. 3. Concentrations of nitrate versus sulfate in cloudwater samples of 1982 and 1983 with mean (std. dev.) of equivalent nitrate/sulfate ratios.

The median values of trace metals (Fe, Pb, Mn, Ni and Cu) concentrations for approximately 100 cloudwater samples collected both years were 520, 260, 46, 36, and 20 ppb, respectively. For iron and lead, the values range from ~100 ppb to several ppm. The occurrences of stratus clouds intercepting inland slopes were linked to on-shore pressure gradients. As a whole, the trace metal concentrations and loadings in the cloud samples reflect the transport of anthropogenic pollutants to elevated sites downwind from their sources.

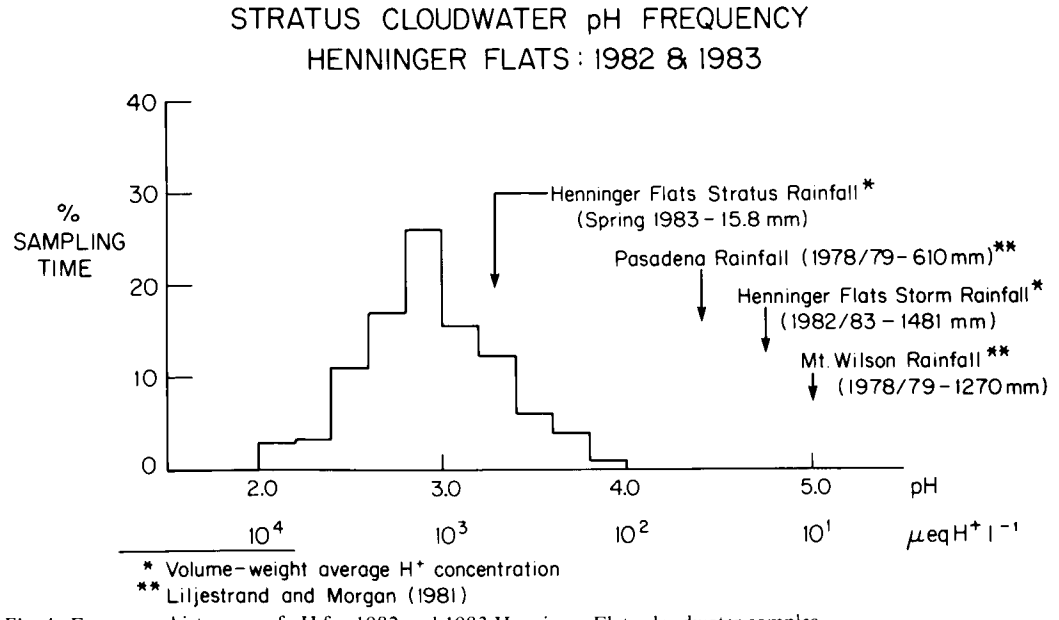

Fig. 4. Frequency histogram of pH for 1982 and 1983 Henninger Flats cloudwater samples.

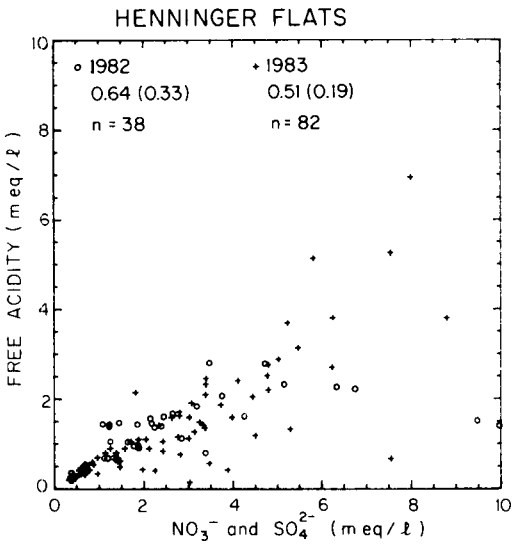

Fig. 5. Free acidity (i.e., $[H^+]$) versus sum of nitrate and sulfate concentrations in cloudwater samples for 1982 and 1983 with mean (std. dev.) of equivalent ratios.

The concentration of S(IV) in cloudwater samples ranged between 1 and 100 μmol l^{-1}, with a two-season median value of 10. Formaldehyde was measured at concentrations 4 to 10 times greater than for S(IV) (median value = 56 μml l^{-1}). These data are given in Munger et al., (1984). Gaseous SO_2 levels at Henninger Flats were measured to be generally 10 ppb or below (Hering and Blumenthal, 1984). Similarly low levels are typical in nearby Pasadena during the spring. The formations of S(IV)-aldehyde adducts in solution led to total aqueous S(IV) concentrations which exceeded the Henry's law solubility for gaseous SO_2 at low pH (Munger et al., 1984), although these were yet a small fraction of aqueous sulfur.

3.2. *Examples of specific events*

Ambient aerosol was sampled prior, during and following several fog episodes in 1983 (Table 2). Aerosol concentrations (μeq m^{-3} of air) measured on Teflon filters were comparable to those of cloudwater samples (Fig. 6). During fog, these samples included droplets as well. Values for aerosol $[H^+]$ concentration were calculated from the ionic charge deficiency. This procedure is justified by the large excess of anions observed and the resulting low aerosol pH predicted. Several points are suggested from these data. First, the acidities of the precursor aerosol were somewhat lower than those measured for cloudwater. Filter samples collected wholly during fog were generally more acidic. Daum et al. (1984) found clear-air aerosol to contain much less acidity than the cloudwater in the eastern United States for samples collected aloft, although they make the caveat that the samples they compare were from different days. Our calculations indicate that much of the cloudwater solute was derived from ambient aerosol scavenged by cloud formation; some but not all of the resultant aqueous acidity is measured in the precursor aerosol. Second, the nitrate-to-sulfate ratios of the afternoon and late evening (non-fog) intervals were usually less than one, while the concentrations of nitrate generally showed a large increase immediately following the onset of fog, wherein the ratio was between 1.5 and 2. Shown in Fig. 6, the aerosol nitrate measured after fog formed increased (June 11) while all the other measured species remained unchanged.

A likely source of additional nitrate is the scavenging of nitric acid vapor by the droplets. Compared to levels measured in non-fog aerosol, the increase in nitrate was around 0.1 to 0.2 μmol m^{-3}, similar to nitric acid values reported for the Los Angeles atmosphere (Spicer et al., 1982). Nitric acid was measured in clear air at Henninger Flats during June 1984 between 0.01 and 0.4 μmol m^{-3} (Waldman, 1985). In all aerosol and cloudwater samples, there was unneutralized acidity. Under these conditions, gaseous ammonia would be completely scavenged by acidic sulfate aerosol. Nitric acid would remain unneutralized and, in clear air, in the gas phase. The increase in suspended liquid water upon fog formation results in 100% scavenging of nitric acid (Jacob and Hoffmann, 1983). Conversely, for dissipating fog conditions, nitric acid would be driven back into the gas phase.

The lower pre-fog concentrations measured could have also been caused by particulate nitrate loss due to ammonium nitrate volatilization from the Teflon filter medium (Appel et al., 1979). For cool, humid conditions at Henninger Flats (e.g. T = 10 °C and R.H. $\geq$ 90%), the equilibrium dissociation constant (K_Y) for NH_4NO_3 is below 0.1 ppb^2 or 1.8×10^{-4} (μmol m^{-3})^2 (Stelson and Seinfeld, 1982). Therefore, during most sample intervals, K_Y would be too low for this to be a significant artifact. It appears that some nitric acid

Table 2. *Ambient aerosol chemical concentrations—Henninger Flats: June 1983*

			μeq m $^{-3}$					cloudwater[d]	
Date & Time	Size[a]	Fog[b]	NH_4^+	NO_3^-	SO_4^{2-}	"pH"[c]	NO_3^-/SO_4^{2-}	pH	NO_3^-/SO_4^{2-}
June 8									
	T	post	0.196	0.067	0.312	"3.11"	0.22		
0000–0600	F		0.189	0.018	0.273			2.71	1.11
	(C)		(0.007)	(0.049)	(0.039)	"3.47"	1.26		
2145–0215	T	fog	0.101	0.294	0.213	"2.74"	1.38		
	F		0.009	0.042	0.086			3.00	1.68
	(C)		(0.092)	(0.252)	(0.127)	"2.86"	1.98		
June 10									
1200–1800	T	pre	0.154	0.070	0.284	"3.25"	0.25		
	F		0.159	0.012	0.265				
	(C)		(0.005)	(0.058)	(0.019)	"3.98"	3.05		
2230–0230	T	pre	0.136	0.073	0.195	"3.39"	0.37		
	F		0.188	0.044	0.190				
	(C)		(0.052)	(0.029)	(0.005)	"3.51"	5.80		
June 11									
0630–1030	T	fog	0.154	0.265	0.185	"2.87"	1.43		
	F		0.050	0.010	0.069			3.01	1.85
	(C)		(0.104)	(0.255)	(0.116)	"2.92"	2.20		
1040–1430	T	fog	0.057	0.105	0.109	"3.22"	0.96		
	F		0.034	0.004	0.045			3.26	1.36
	(C)		(0.023)	(0.101)	(0.064)	"3.27"	1.58		
June 12									
0800–1200	T	fog/post	0.200	0.201	0.197	"3.40"	1.02		
	F		0.041	0.044	0.082			3.57	1.43
	(C)		(0.159)	(0.151)	(0.115)	"3.82"	1.31		
June 19									
0045–0600	T	patchy fog	0.027	0.068	0.100	"3.33"	0.68	2.87	1.65
June 21									
0835–1045	T	patchy fog	0.257	0.269	0.480	"2.95"	0.56		
	F		0.242	0.057	0.267			2.67	na
	(C)		(0.015)	(0.212)	(0.213)	"3.05"	1.00		
June 22									
0430–0830	T	fog/post	0.243	0.141	0.262	"3.46"	0.54		
	F		0.213	0.098	0.229			3.09	2.50
	(C)		(0.030)	(0.043)	(0.033)	"4.52"	1.30		

[a] T, total particulate (open-faced filter); F, fine particulate ($d_p < 3$ μm); (C), coarse: T minus F.
[b] Conditions during sampling relative to fog episode.
[c] "pH" calculated assuming H^+ balanced charge deficiency of major ions and LWC = 0.2 g m $^{-3}$.
[d] LWC and time-weighted average values for cloudwater samples relative to b; nitrate/sulfate ratios are on equivalent basis.

loss from the filters during patchy and dissipating fogs (e.g., June 21 and 22) led to NO_3^-/SO_4^{2-} values below cloudwater ratios. A third possibility exists by which the noted increase in nitrate concentrations were due to its advection to the site. However, there was no increase in measured gaseous pollutants (SO_2, NO_x and O_3) following the onset of the fog (Hering and Blumenthal, 1984).

Prior to the fog, most of the particulate solute, especially sulfate, was measured in the fine (<3 μm) size class. In dense fog, very little of the particulate solute remained in the fine-size class. However, the proportion of sulfate found in the

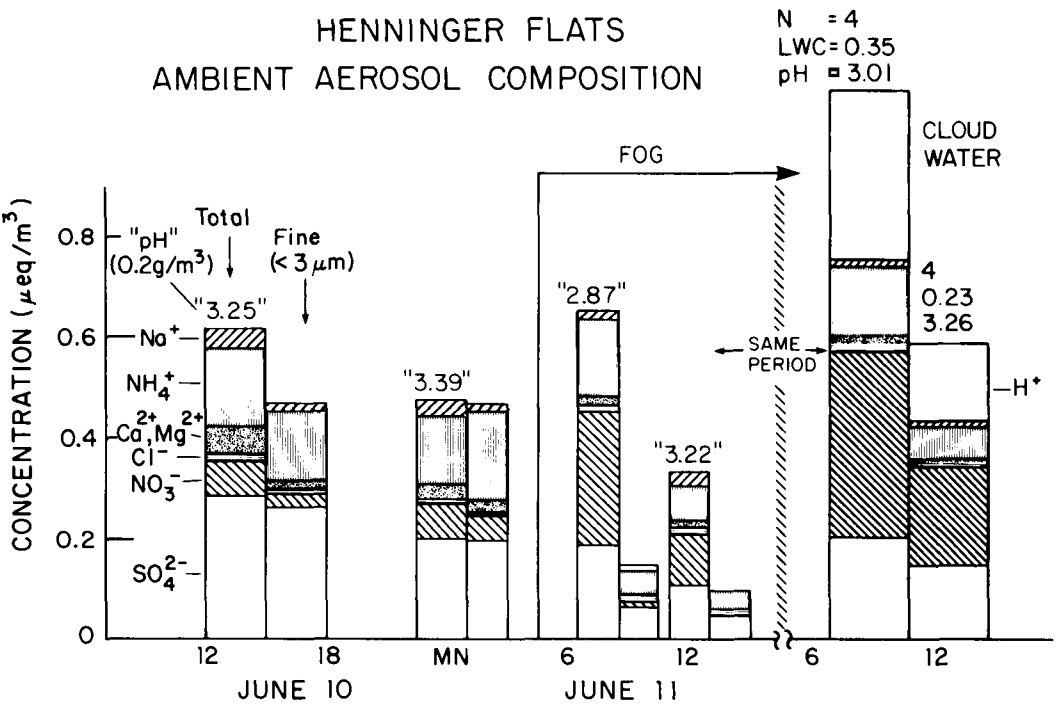

Fig. 6. Ambient aerosol composition for June 10–11, 1983. Total and fine ($d_p < 3$ μm) particulate concentrations given are for each sample interval. Time-weighted solute concentrations for cloudwater samples are shown for the latter two intervals.

fine-size fraction of the filter samples (1/3 to 1/2) was greater than for nitrate. This difference is primarily due to the presence of precursor nitrate in the air as nitric acid which is subsequently absorbed into fog droplets. Also, as nitrate and sulfate salts are highly hygroscopic, the difference in the portion which was activated into droplets would be a function of particle size. The model of Bassett and Seinfeld (1984) predicts that nitric acid will be more favorably absorbed by larger aerosol, due to the Kelvin effect. Previous findings that nitrate is associated with larger-sized aerosol (Appel et al., 1978) would support an interpretation that particulate nitrate was more completely scavenged by droplet activation. Cloudwater samples collected during post-precipitation intervals generally had the lowest nitrate-to-sulfate ratios. As suggested above, this could be caused by mechanisms which scavenge (and deposit) nitrate more effectively than sulfate.

Concentration, LWC, and solute mass loading profiles for cloudwater samples from June 11 and 12, 1983 are shown in Fig. 7. During the first several hours of sampling, as the marine air permeated the forest, the fog was patchy, and the LWC fluctuated dramatically. In addition, there were brief periods of complete dissipation at the onset of this fog episode when deactivation of cloud droplets would remove cloudwater solute mass to the haze-size range, below the collector size-cut. For these first few intervals, the RAC-derived value (estimated from the entire sampling period) underestimated LWC for the fog actually collected. Thus, a representative indication of the cloudwater solute loading is difficult to determine for time-averaged samples in locally patchy fogs.

After 0700, fog became more stable at the site (Fig. 7b), and the solute loading remained fairly constant for the next 4 to 5 hours (Fig. 7c). A slight drizzle began at 0800, intensifying to a measurable rate in the mid-afternoon. Often, drizzle-size drops do not fall far below the cloud base before they evaporate. During the afternoon (June 11), 5.8 mm of rainfall was measured at the site, which was

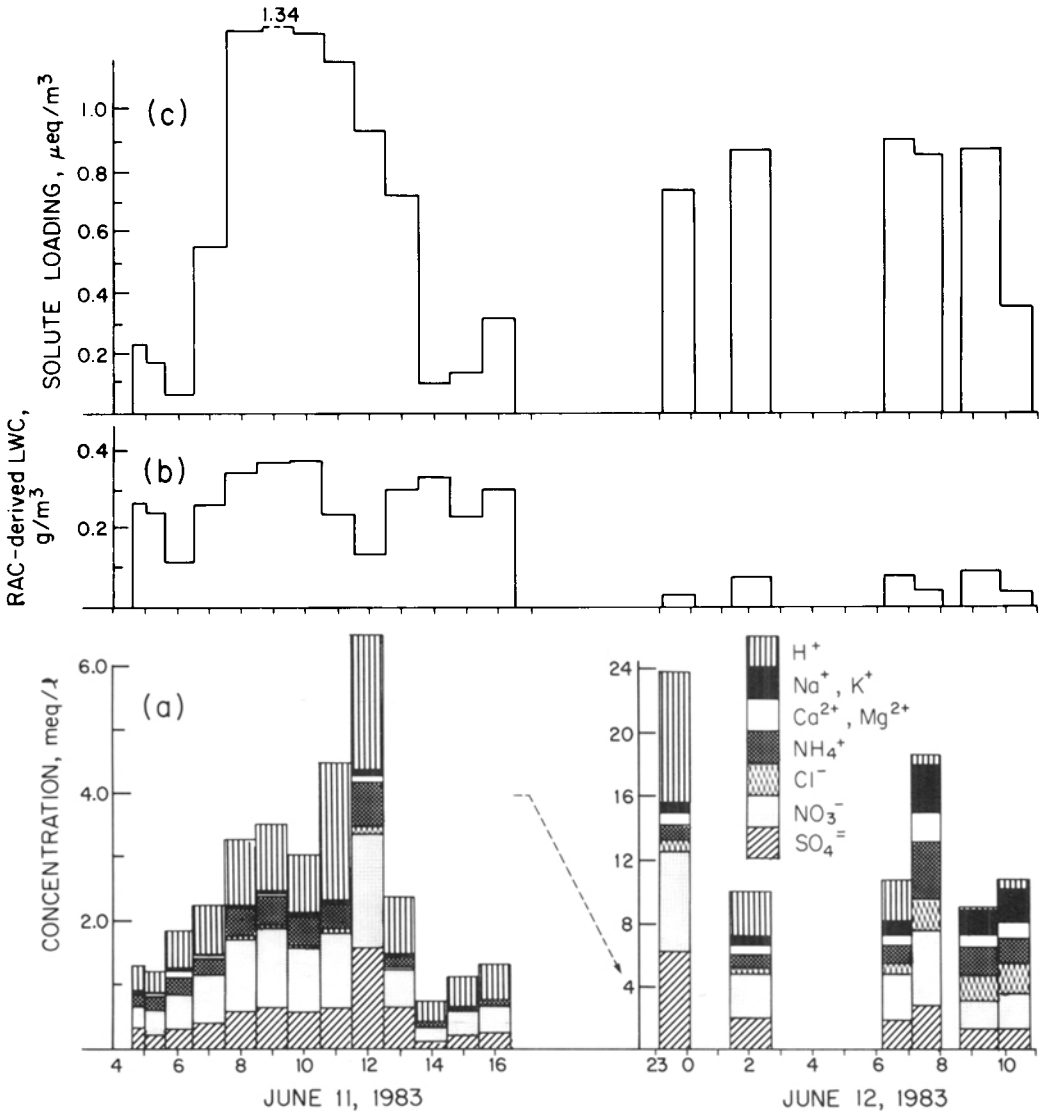

Fig. 7. (a) Concentration, (b) LWC, and (c) ambient solute loading for sequential cloudwater samples on June 11 and 12, 1982. Note the change in scale (a). A slight drizzle began 0800 on June 11, intensifying after 1200 and ending by early evening.

above the cloud base, compared to the trace (<0.25 mm) measured ~500 m below the base in Pasadena. Coincident with afternoon drizzle was a drop in ambient solute concentrations (see Fig. 6 and 7c). The total solute deposited in the drizzle (see subsequent section) was several times the product of aerosol concentration and cloud height, which indicates a continuing source of solutes. Advection of pollutant-laden cloud air to the mountain slope adds to the amount deposited in the rainfall there, while upwind over the lower basin no preciptation was occurring. Also following the onset of rainfall, the mass median diameter for measured cloud droplet spectra became lower. The collection efficiencies of cloud droplets by drizzle-size drops falling to the ground increases for larger droplets (Pruppacher and Klett, 1978). Hudson and Rogers (1984) have shown that a significant fraction of

the larger nuclei are found in the larger droplets. The depletion of larger, cloud droplets, taken with the magnitude of solute deposition measured in the drizzle, lends further support to the interpretation that the drop in cloudwater solute loading was caused by its depletion by precipitation scavenging.

The fog continued with fairly uniform LWC through that day—drizzle ceasing in the late afternoon—and into the following morning. Cloudwater sampling was discontinued until 2300. Two intermittent samples were collected before continuous sampling was resumed at 0600 on June 12. For June 12 samples, the ambient solute loading was elevated to the pre-drizzle level—aqueous concentrations were much higher with fluctuations mirrored by commensurately lower LWC. Similarly, the solute measured in fog on filters was greater (Table 2). The large-scale eddy circulation which had deepened the marine layer in the previous afternoon had weakened. The increase in pollutant levels in the cloud was partially a reflection of this decrease in the mixing depth. Also, as the drizzle had ceased, advected pollutants in the cloud air would not be locally depleted. In the morning, the cloudwater samples became progressively less acidic, and equimolar Na^+ and Cl^- increases occurred. This latter point suggests that air of greater marine character was advected to the site. The roles of vertical mixing and ventilation within stratus clouds and fogs are major uncertainties. Until we can better quantify the transport component of cloud/fog dynamics at a given sampling site, our explanations remain speculative. Finally, the drop in solute loading for the last sample accompanied evaporation of fog droplets.

3.3 *Deposition: measurements and calculations*

3.3.1. Storm and stratus rain. Rainfall at Henninger Flats was collected and analyzed from November 1982 to June 1983. In Table 3, the wet deposition is split between storm (A) and (B) spring stratus events. The 1982–83 season (October 1 to September 30) was above average rainfall—the wettest on record at Henninger Flats: 1660 mm compared to an average of 670 mm. Pasadena and Mt. Wilson deposition (from 1978–79 data) are presented for comparison. Because of the high frequency and water flux per storm event, the

Table 3. *Wet deposition—Henninger Flats: October 1982 to July 1983*

			meq m^{-2}								
Month	#	mm	H^+	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Cl	NO_3	SO_4^{2-}
A. Storms[a]											
Sum (mean[d])	34	1480	27.8	20.6	1.2	12.1	4.9	7.2	25.2	18.4	23.4
			(18.8)	(13.9)	(0.8)	(8.2)	(3.3)	(4.8)	(17.0)	(12.4)	(15.8)
B. Stratus[b]											
Sum (mean[d])	6	15.8	8.33	0.87	0.13	1.68	1.24	0.64	1.30	7.40	5.45
			(526)	(55)	(8)	(106)	(78)	(41)	(82)	(467)	(344)
$\frac{B}{A+B} \times 100$		1.1	23.1	4.1	9.7	12.2	20.2	8.2	4.9	28.7	18.9
1978/1979[c]											
Pasadena		610	23.8	14.6	1.0	12.8	4.1	4.4	17.1	18.9	23.8
(mean[d])			(39)	(24)	(1.7)	(21)	(6.7)	(7.3)	(28)	(31)	(39)
Mt. Wilson		1270	12.7	33.0	2.2	45.7	11.8	8.4	35.6	29.2	30.8
(mean[d])			(10)	(26)	(1.7)	(36)	(9.3)	(6.6)	(28)	(23)	(40)

[a] Five major storms (total = 250 mm) and several light rains (<10 mm) between Oct. and Apr. were missed. Standard rainfall gauge values were used to calculate individual storm deposition when portion of rainfall was missed by collector. The volume-weighted concentrations were used to determine total storm deposition.

[b] Actually, two stratus events (total = 13.3 mm) were collected; four additional trace events (total = 2.5 mm) were assumed to have similar concentrations to calculate total stratus deposition.

[c] Liljestrand and Morgan (1981).

[d] Volume-weighted mean concentration (μeq l^{-1}).

volume-weighted mean concentrations (A) were lower than in the earlier year. Stratus events (i.e., drizzle or light rainfall) occurred within a developed marine layer, similar to that which led to stratus cloudiness and fog on mountain slopes but with more intense deepening. The ionic concentrations of these light rains were dramatically higher than for the storm events, but in a range somewhat less concentrated and acidic than the cloudwater samples. Morgan and Liljestrand (1980) noted similarly higher concentrations in sparser rains they measured in Pasadena. Brewer et al. (1983) reported a similar relationship between fog and "mist" (i.e. drizzle) samples at several Los Angeles locations.

The meteorology is an important factor to consider in comparing the precipitation types. Most wintertime storms are associated with weather systems which advect moist, unstable oceanic air with fairly intense convective activity extending up to >5000 m (Keith, 1980). On the other hand, drizzle and fog events usually occur within a developed marine layer constrained by a strong temperature inversion aloft. This limits the vertical extent of mixing; thus, stratus cloud droplets form and can have longer residence times in the polluted atmosphere. The mean pH values for stratus and storm rainwater are compared to cloudwater samples in Fig. 4. The fog → drizzle → rain hierarchy of solute concentration also reflects the relationship between droplet size and dilution. The growth of non-freezing cloud droplets to a size with appreciable sedimentation velocity occurs solely by condensation of water vapor for sizes below 50 μm diameter; subsequently both coalescence and condensation lead to drizzle (0.2 to 0.5 mm) and raindrop (>0.05 mm) sizes, depending upon the intensity of vertical motion (Pruppacher and Klett, 1978).

Stratus events led to solute deposition which was disproportionate to the water flux. While accounting for ~1% of measured rainfall, nearly 20% or more of H^+, NO_3^- and SO_4^{2-} were deposited in less than 16 mm precipitation. Na^+ and Cl^- were much less enhanced in stratus rainfall. The winter storms responsible for most of the precipitation form over the eastern Pacific Ocean. They are more effective at generating and transporting sea salt aerosol due to their greater convective activity. For stratus events, the enhancement of H^+ and NO_3^- was greatest and, for NH_4^+ and SO_4^{2-}, it was somewhat less. The difference in nitrate/sulfate ratios for stratus (1.4) versus storm (0.8) events is a further indication of the meterological and seasonal variation in SO_2 and NO_x oxidation and transport.

3.3.2. *Bulk deposition and throughfall.* For our program, bulk deposition was collected with open buckets. These provided large collection areas, minimized resuspension (relative to flat surfaces) and were convenient to use and rinse. Standard 4-gallon, polyethylene buckets (open area = 566 cm^2) were placed with the rim at least 1 meter above the ground in the vicinity of the nursery (see Fig. 1). One bucket was placed beneath a dense stand of Coulter pine (*Pinus coulteri*). The containers were extracted with 0 to 500 ml of H_2O, depending on the exposure duration and precipitation amount.

Surrogate surface methods, such as flat plates and open containers, remain controversial due to the variability of their results and the uncertainty in extrapolation of specific results to a regional value. From intercomparison of surrogate surfaces (Dolske and Gatz, 1984; Dasch, 1983), buckets were shown to give flux values which were sensitive to ambient aerosol sulfate levels. Dry deposition of SO_2 and NO_x has been reported to be inconsequential for the plastic buckets (Dasch, 1983); however, gaseous nitric acid might be expected to contribute to the measured deposition because of its reactivity.

There are uncertainties in interpreting these data: for example, atmospheric conditions for the sampling intervals were not well known with respect to aerosol size spectra, pollutant fractionation, or micrometeorology. For simple topography, a very detailed data set sould be required; for complex terrain, the problem is almost intractable. Rather, the bulk deposition measurements are presented to provide a relative measure of solute deposition under varying, ambient conditions.

Overall, bulk deposition for most intervals with precipitation was significantly greater than for intervals with none (Table 4). For example, the deposition rates for H^+, NH_4^+, NO_3^- and SO_4^{2-}, averaged for the two intervals with measurable rainfall (May 26–June 3 and June 9–13), were 10 or more times that of the other intervals listed. The dry-only deposition (i.e., with the measured wet-only values subtracted) was also greater for those intervals. These coincided with stratus clouds and fog. This indicated to us, as noted in the previous section, that trace precipitation (not measured in

Table 4. *Bulk deposition and throughfall—Henninger Flats: May–July 1983*

		meq m^{-2} (std. dev.)									
Interval	Location[a]	"H^+"[b]	Na^+	K^+	NH_4^+		Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}
May 12–19											
(168 h)	O (3)	0.0 (0.0)	0.52 (0.08)	0.35 (0.13)	0.39	(0.37)	0.30 (0.11)	0.40 (0.24)	0.16 (0.08)	0.78 (0.10)	0.59 (0.26)
	C (1)	0.0	0.16	0.09	0.07		0.31	0.19	0.14	0.43	0.17
May 19–26											
(162 h)	O (2)	0.10 (0.10)	0.05 (0.01)	0.10 (0.08)	0.20	(0.23)	0.21 (0.02)	0.09 (0.04)	0.10 (0.10)	0.47 (0.08)	0.10 (0.03)
	C (1)	0.18	0.05	0.07	0.05		0.21	0.07	0.04	0.45	0.17
May 26–June 3											
(191 h)	O (3)	4.69 (0.87)	2.04 (0.25)	0.30 (0.17)	2.28	(0.69)	0.81 (0.02)	0.91 (0.27)	1.87 (0.04)	5.49 (0.06)	4.42 (0.35)
	C (1)	4.41	3.71	5.71	3.48		4.35	3.93	2.96	14.5	5.50
Wet only– 15 mm		3.83	0.56	0.09	0.89		0.74	0.42	0.63	3.60	2.80
June 3–9											
(156 h)	O (3)	0.55 (0.60)	0.28 (0.03)	0.19 (0.10)	0.21	(0.17)	0.66 (0.04)	0.34 (0.10)	0.20 (0.03)	1.05 (0.40)	0.73 (0.34)
	C (1)	0.47	0.16	0.07	0.24		0.36	0.13	0.10	0.80	0.37
Wet only– 0.5 mm[c]		0.26	0.03	0.00	0.05		0.04	0.02	0.04	0.23	0.17
June 9–13											
(94 h)	O (3)	3.34 (0.64)	0.41 (0.15)	0.12 (0.10)	1.28	(0.21)	0.54 (0.20)	0.26 (0.13)	0.33 (0.16)	4.07 (0.99)	2.64 (0.56)
	C (1)	4.59	1.34	1.65	1.59		2.06	1.44	0.90	8.55	4.04
Wet only– 5.8 mm		3.38	0.18	0.02	0.56		0.42	0.21	0.46	2.76	1.85
June 13–19											
(135 h)	O (1)	0.0	0.09	0.14	0.08		0.20	0.14	0.12	0.22	0.11
June 19–July 11											
(531 h)	O (2)	0.15 (0.08)	1.08 (0.01)	0.15 (0.05)	0.81	(0.02)	0.92 (0.08)	0.85 (0.09)	0.11 (0.0)	1.57 (0.11)	1.55 (0.13)
Wet only– 2.0 mm[c]		1.05	0.11	0.02	0.21		0.16	0.08	0.16	0.93	0.69
July 11–25											
(342 h)	O (2)	0.05 (0.01)	0.26 (0.0)	0.07 (0.01)	0.16	(0.11)	0.24 (0.18)	0.16 (0.0)	0.13 (0.16)	0.65 (0.05)	0.19 (0.08)

[a] O = Open; C = Under Canopy; (# replicates).
[b] "H^+" deposition from pH of bucket extraction or precipitation sample.
[c] Wet only deposition calculated from measured trace rainfall × mean stratus (B) concentration (see Table 3).

standard rainfall gages) accompanying these low clouds had enhanced solute flux associated with it.

During dry periods, the below-canopy sample had generally lower pollutant deposition compared to open collectors. This reduction may be due to the interception of material to the canopy alone, or the suppression of turbulent transport below the canopy as well. It also appeared that some of this material eventually was deposited as throughfall when appreciable rainfall occurred (cf. June 3–9 to June 9–13). However, some of the additional cations had likely leached from the pine needles.

3.3.3. *Calculation of fog precipitation.* Fog droplet capture by the forest canopy has been recognized as an important hydrologic input. Hori (1953) and co-workers conducted extensive research on the mechanisms and efficiency of droplet capture. Lovett (1984) modeled the transfer of liquid water to the forest canopy in fog-laden winds. Compared to the deposition of dry aerosol (Sehmel, 1974), the capture of fog droplets is significantly more efficient. The parameters that control the rate of deposition are the wind speed and turbulence, canopy and leaf geometries, and fog LWC and droplet size distribution. Lovett calculated water deposition rates, chiefly by impaction to the upper 3 m of the canopy, which varied linearly from 0.2 to 1.2 mm h^{-1} for canopy-top wind speeds of 2 to 10 m s^{-1}. From collection on natural and surrogate surfaces, Yosida (1953) reported an overall average rate of 0.5 mm h^{-1} for fogwater capture by the forest canopy. Fog-induced water flux deposition can vary greatly, even tree-to-tree (e.g. Oberlander, 1956). For sparsely forested areas and chaparral, the average would be expected to be lower. Dollard et al. (1983) estimated a mean cloud drop flux of 0.07 mm h^{-1} to shortgrass by eddy turbulence and sedimentation in fog, based on micrometeorological techniques.

Direct measurement of this deposition was not made during this study. Instead, we assumed a water deposition rate of 0.2 mm h^{-1} to calculate

approximate values of fog-induced fluxes for cloudwater with the measured composition. Henninger Flats has a relatively dense, tall canopy. Canopy-top data were not measured. The LWC at canopy-top would be somewhat higher than at the ground (Lovett, 1984); aqueous concentrations would be commensurately lower at elevated locations. In the nursery, winds were generally <1 m s^{-1}; wind speeds measured just downslope of the site were $\sim$1–2 m s^{-1}, hence a conservative water deposition rate was used. Using the above rate (0.2 mm h^{-1}) with the median [H$^+$] of 1150 μeq l^{-1} gave an average rate equal to 230 μeq m^{-2} h^{-1}. Also using the median values for 1982 and 1983 data, nitrate and sulfate deposition rates were calculated to be 300 and 170 μeq m^{-2} h^{-1}, respectively.

3.3.4. *Comparison of pollutant wet deposition pathways.* It is difficult to generalize about the frequency and duration of cloud interception within the Los Angeles basin. It is subject to spatial and temporal variability as well as year-to-year fluctuation. The presence of marine layer clouds and fog are persistent phenomena in coastal southern California, especially during spring and summer (Keith, 1980). From a daily record kept by rangers at Henninger Flats (Los Angeles County Fire Department, Forestry Bureau, unpublished meteorological records, 1983), the median number of times dense fog was observed at 8 a.m. was 30 per year (range = 8 to 55) and 12 during the May/June period for 1970–83. However, clouds are as often observed to intercept the mountain slope less than several hundred meters above or below the site. Further, clearing prior to the morning observation often occurs. Hence, at an inland location, the Henninger Flats observations are likely a conservative estimate of the frequency that low-lying clouds intercept coastal mountain slopes in the Los Angeles area. Both 1982 and 1983 were above normal for fog, with 31 and 18 morning observations of fog during each May/June period, respectively. During our two years of monitoring, over 120 fog-hours were sampled on 23 days or approximately 5 hours per event.

Assuming deposition rates as in the previous section with 150 hours of cloud interception per year (i.e., 30 events times an average of 5 hours per event), the product gave an annual total of 35 meq H$^+$ m^{-2}. Similar calculations for NH_4^+, NO_3^-, and SO_4^{2-} yield 17, 45, and 24 meq m^{-2}, respectively; for lead, 8 mg m^{-2} deposition annually is calculated. Though the preceding calculations are based on limited data and rough estimates, they are intended to demonstrate the order of magnitude that cloud droplet processes may contribute to the acidic deposition in this urban-impacted mountain environment. Comparing these with measured precipitation (Table 3), cloud interception could deliver up to half the total wet deposition. At coastal sites with less rainfall and greater fog frequency, the effect could be greater.

4. Cloudwater interactions with foliar surfaces

Part of our motivation to sample cloudwater at Henninger Flats was the observation in the spring 1982 of an unseasonably high number of pine trees, especially Monterey-Knobcone (*Pinus radiata* × *attenuata* hybrid) which exhibited necrotic needles (M. Gubrud, Senior Deputy Ranger, Los Angeles Fire Department, Forestry Bureau, private communication, 1982). Normally, needle necrosis is observed in the late summer and early autumn, due to the high oxidant levels in the Los Angeles basin (Richards et al., 1968).

4.1. *Measurements*

To better understand the nature of its interaction with plant tissue, cloudwater was removed from pine needles where it had naturally deposited during several fog events. These samples were aggregated from several hundreds of individual drops (d = 1 to 2 mm) taken from the lower reaches ($\sim$1.5 m) of a variety of individual pine trees. All the pine needles from which samples were removed showed some degree of browning at the tips where the cloudwater had collected, but were otherwise green and healthy. In general, these samples were found to be as acidic though often more concentrated than the suspended cloudwater. In Fig. 8, the equivalent ratio of major ions to sulfate are presented for tree drop samples and for cloudwater samples collected simultaneously. The measured concentrations can be derived from comparing the ratio with the [SO_4^{2-}] given in the figure. Nitrate was 2 or more times greater than sulfate for these samples. The highest ionic con-

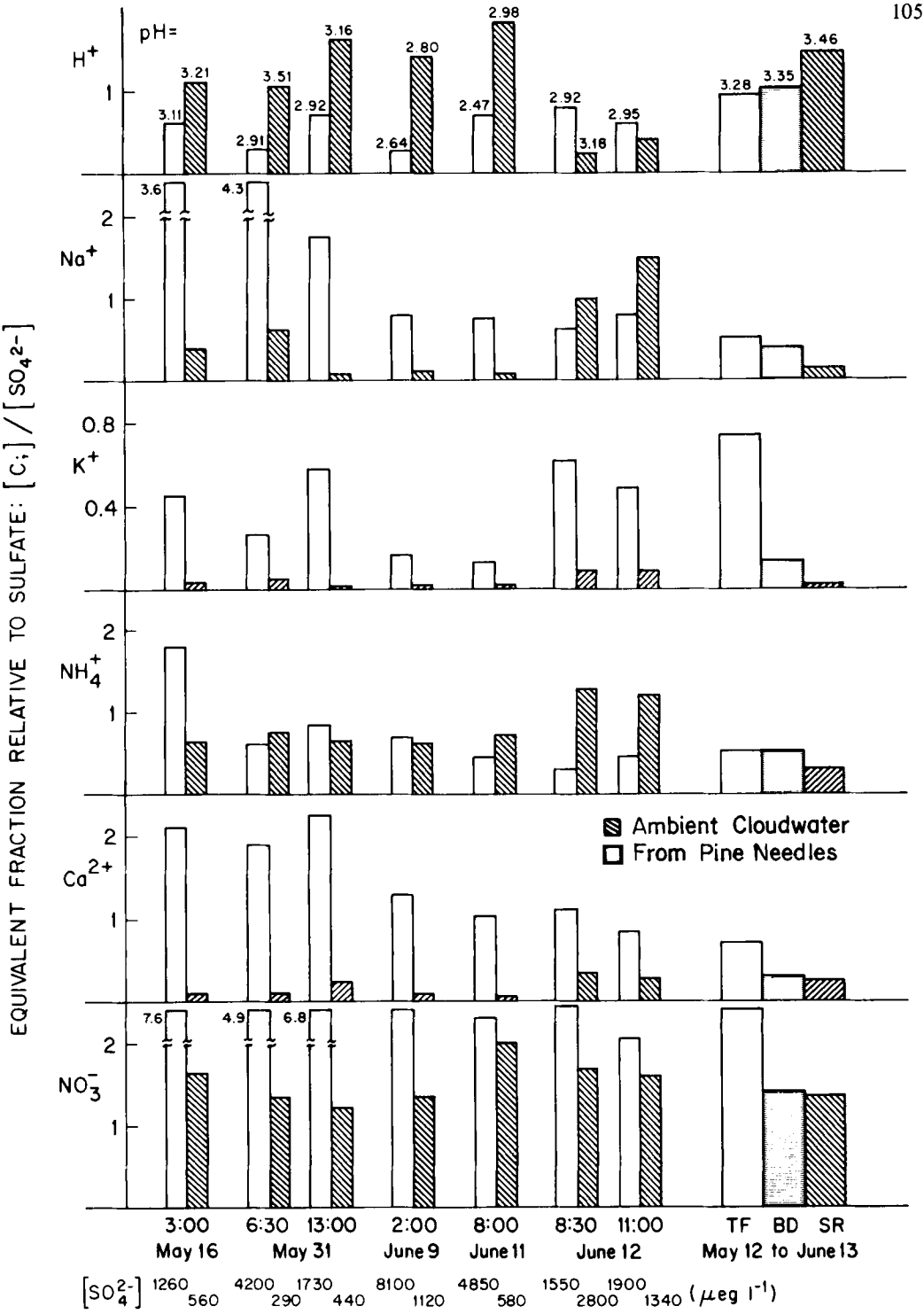

Fig. 8. Equivalent fractions of ionic species relative to sulfate in cloudwater removed from pine needles (open) and ambient cloudwater (shaded) collected simultaneously in 1983. TF is throughfall; BD is bulk deposition; and SR is stratus rainwater (see Table 4).

centrations were found for intervals preceeded by dry periods (e.g., May 16 and May 31). Samples for intervals following rainfall or a long duration of fog had concentrations generally lower compared to the earlier samples. The fractions of Na^+, K^+, Ca^{2+}, and Mg^{2+} in the fog drops were much higher than in any of the fogwater samples.

4.2. *Discussion*

Leaching of internal leaf tissue cations, especially K^+, by aqueous proton could explain their enhanced ratios. Scherbatskoy and Klein (1983) reported leaching of K^+, Ca^{2+}, and amino acids for birch and spruce foliage exposed to acidic (pH = 4.3 and 2.8) mists. They also suggested that the increase in leachate pH compared to the applied mists involved cation exchange process. Hoffman et al. (1980) indicated that proton exchange with cations was negligible as rain (pH ~4) penetrated chestnut canopies, for the total acidity of rainwater was conserved during throughfall, with weak acids exchanging for strong acids. This may be the case for moderate acidity, but at higher $[H^+]$ specific leaf injury could occur, accompanied or, more likely, caused by proton exchange. Cronan and Reiner (1983) also reported enhancement of basic cations in coniferous and hardwood throughfall with concurrent neutralization of precipitation (pH = 4.1). They proposed both proton exchange and Bronsted base leaching in the canopy as important processes. Throughfall measured during stratus rainfall (see Fig. 8) demonstrated similar enhancement of basic cations, however, with nitrate and acidity enhanced as well. The release of accumulated dry-deposited acidic aerosol and nitric acid was likely important.

Without further research, it is not possible to confirm a direct relationship between acidic cloudwater and needle symptoms observed at Henninger Flats. However, similar damage to leaf surfaces has been reported in exposure studies. In simulated acid rain experiments, Haines et al. (1980) found a threshold of leaf damage for most species tested in a pH range 2.5 to 2.0 and for *Pinus strobus* needles at pH 1.0 to 0.5. Wood and Bormann (1974) observed foliar tissue damage at pH 3 for misting of yellow birch seedlings; significant growth decreases occurred when acidic exposure (pH 2.3) was initiated during the germination stage. Thomas et al. (1952) reported cases in which plant injury was not initially caused by concentrated H_2SO_4 aerosol—apparently due to its high surface tension—but followed surface wetting by fog.

Cloudwater capture may represent a more severe threat to plant tissue than deposition accompanying rainfall or by dry particle deposition alone, because it subjects plant surfaces to much higher aqueous concentrations and acidities. Dry deposition of pollutant gases (e.g., SO_2) can also lead to acidic solutions, however, these affecting internal tissue (Hallgren, 1978). Leaf surface wetting may be a critical component of the interaction between foliar membranes and deposited pollutants. This potential has been raised by Lindburg et al. (1982) with respect to the wetting of metal particles they monitored on dry leaf surfaces. Furthermore, surface wetting greatly reduces particle rebound (Chamberlain, 1967) and enhances SO_2 uptake by pine needles (Garland and Branson, 1977).

5. Summary

Highly concentrated, acidic stratus cloudwater was monitored as it intercepted a Los Angeles pine forest. Observed pH values ranged from 2.06 to 3.87 for samples (n = 128) collected on 8 days in June 1982 and 15 days in May/June 1983. The median value was below pH 3 for both seasons' data. The ratio of nitrate/sulfate in cloudwater samples was between 1.5 and 2; rainwater at the same site had a ratio of approximately 1. About half of the nitrate and sulfate measured in the cloudwater was not neutralized. The solute mass per cubic meter of air in the cloudwater was of the same magnitude as for aerosol samples collected before, during and after fog episodes. The nitrate/sulfate ratio of the dry aerosol was lower than in the cloudwater; the additional nitrate is believed to be derived from dissolution of gaseous nitric acid by cloud droplets. Overall, a higher fraction of precursor nitrate (aerosol and gaseous) than sulfate aerosol appears to be scavenged by the cloud droplets.

Wet deposition at Henninger Flats in 1982–83 was comparable to the value for Pasadena in 1978–79, even though the water flux was more than twice as great. The greater frequency and rainfall amount per storm in the recent year is believed to have led to the lower volume-weighted

mean concentrations in the Henninger Flats precipitation. The solute deposition with several light, spring rains (summing to ~1% of annual rainfall) was a disproportionate fraction of the annual total: H^+, NO_3^-, and SO_4^{2-} were ~20% or more.

Based on a reasonable estimate of fog precipitation, deposition of sulfate, nitrate and free acidity due to intercepted stratus clouds may be of comparable magnitude as that due to the incident rainfall at Henninger Flats. Fog and stratus precipitation, though not previously considered on the regional scale, appears to be a seasonally important vector for pollutant deposition in the Los Angeles basin.

Cloudwater that had deposited on local pine needles was collected and found to be in general more concentrated and with acidity comparable to suspended cloudwater. Enhancement of cations, especially K^+, is believed to be due to leaching from foliar surfaces. Enhancement was also found in throughfall samples collected during stratus rainfall. Injury to sensitive plant tissue has been reported in the literature by exposure to similarly acidic solutions.

6. Acknowledgements

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